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Spectrophotometric Determination of Iron(III) after Separation by Adsorption of its Pyrrolidinedithiocarbamate on Naphthalene

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A method is presented for the spectrophotometric determination of trace amounts of iron(III) after adsorption of its pyrrolidinedithiocarbamate with microcrystalline naphthalene. Iron(III) forms a stable chelate with pyrrolidinedithiocarbamate ammonium salt and this chelate is quantitatively adsorbed onto microcrystalline naphthalene at room temperature in the pH range of 2.9-6.6. The mixture of the chelate and naphthalene is dissolved in chloroform. The chelate in naphthalene-chloroform solution obeys Beer's law over the range 2.3-49 μg of iron(III) in 10 ml of chloroform. The molar absorptivity is 1.1×10^4 $l \cdot mol^{-1} \cdot cm^{-1}$ at 357 nm, the sensitivity being 4.9×10^{-3} $\mu g/cm^2$ for the absorbance of 0.001. The relative standard deviation for the present analysis of iron(III) is 1.0% for ten determinations. In the present experiments, the effect of variables such as pH, amounts of reagent and naphthalene, digestion and shaking time and diverse ions have been examined. The method has been applied to the determination of iron(III) in reference and environmental samples and results compared with 1,10-phenanthroline method.

1 Introduction

Ammonium pyrrolidinedithiocarbamate(abbreviated as APDC) reacts with many metal ions to form water-insoluble chelates. These chelates have been widely employed for the gravimetry of Nb[1] and Te[2], solvent extraction-spectrophotometry of Cu[3], As[4], Sn, Sb, Bi and MIBK extraction-atomic absorption spectrophotometry of Cu[5], Ni[6], Te[7),8], Cr[9], Zn and Pb.

Recently we have developed a new method of analysis involving adsorption of metal chelates onto microcrystalline naphthalene and their subsequent spectrophotometric determinations, and demonstrated for palladium[10] and nickel[11] with α-furildioxime and copper[12] with Ammonium Pyrrolidinedithiocarbamate.

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In the present work, APDC as a chelating reagent was chosen for the determination of iron(III). The procedure was successfully applied for the determination of iron(III) in the reference materials and environmental samples.

2 Experimental method

2.1 Reagents

Standard iron(III) solution, 10 ppm. Prepared by diluting 10 ml of standard iron(III) solution(1000 ppm, Wako Pure Chemical Industries, Osaka, Japan) to 1000 ml with deionized water.

APDC solution, 0.2%. Prepared by dissolving 0.2 g of APDC in 100 ml of water.

Naphthalene acetone solution, 20%. Prepared by dissolving 20 g of naphthalene in acetone and diluting to 100 ml.

Buffer solutions. Prepared by mixing 1M acetic acid and 1M ammonium acetate solution for pH 3-6; 1M aqueous ammonia and 1M ammonium acetate solution for pH 8-11.

Naphthalene, acetone and all other reagents were of analytical reagent grade, and were used without further purification.

2.2 Apparatus

A Hitachi Model 200-20 double beam spectrophotometer was used for the absorbance measurements.

All pH measurements were done with a Toa-Dempa, HM-5A, pH meter, equipped with a combined calomel and glass electrode assembly.

The naphthalene was dried with a Tabai Model K-2 dryer(Tabai Mfg. Ltd., Japan).

2.3 Procedure

Transfer about 40 ml of sample solution containing 30 μg of iron(III) to a tightly stoppered Erlenmeyer flask, add 2.0 ml of 0.2% APDC solution and adjust pH of the solution to 4.7 with 2.0 ml of the buffer solution. Mix the solution well and stand for 20 min at 20-25°C. Transfer into this solution as fast as possible 2.0 ml of 20% naphthalene solution using a small nozzled pipet attached to a rubber bulb, and shake vigorously for 1.5 min. Separate the solid by filtration using a filter paper(e.g., No5C, Toyo Roshi Co. Japan) placed flat on a filter plate in a funnel, or through a sintered glass filter(No2). Wash with water and dry at 50-60°C in a dryer. Then dissolve the product in chloroform and make up to 10 ml. Measure the absorbance of solution in a 10-mm glass cell at 357 nm against a reagent blank perpared similarly.

3 Results and discussion

3.1 Absorption spectra

Sample solution containing 30 μg of iron(III), 2.0 ml of 0.2% APDC solution and 2.0 ml of the buffer solution was prepared by the procedure, and the adsorption of the chelate was performed. Figure 1 shows the absorption spectra of APDC and iron(III)-APDC chelate in naphthalene-chloroform solution. The absorption spectra was measured in the range of 330-650 nm against water. The iron(III) chelate has three peaks at 357, 500 and 590 nm, whereas the reagent APDC is almost negligible absorption above 350 nm. therefore, 357 nm was chosen as the most sensitive wavelength.

3.2 Effect of pH

The relationship between the absorbance and the pH of the solution after adsorption was investigated in the pH range 1.0-8.8. The result is shown in Fig.2. From the experimental data, the absorbance of the iron(III)-APDC chelate increased sharply with increasing pH, reached the maximum and constant over the range 2.9-6.6, and decreased sharply above pH 6.6. Therefore, the pH of the solution was adjusted to 4.7 for the absorbance measurements.

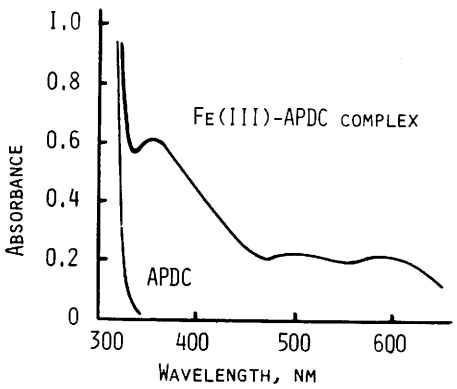

FIG. 1 ABSORPTION SPECTRA OF APDC AND IRON(III) COMPLEX IN NAPHTHALENE-$CHCl_3$
Fe(III) : 30 μg ; pH : 4.7 ; DIGESTION TIME : 15 MIN ; 0.2% APDC : 2.0 ml
REFERENCE : WATER

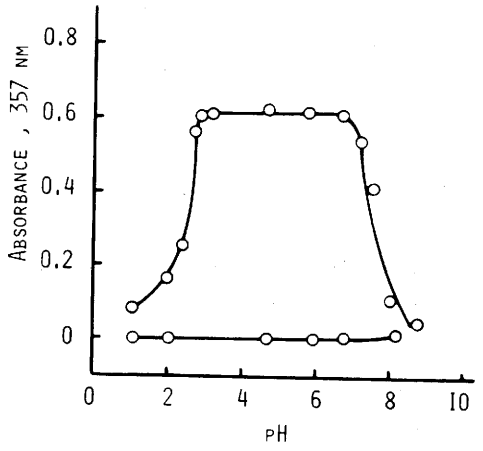

FIG. 2 EFFECT OF pH
Fe(III) : 30 μg ; 0.2% APDC : 2.0 ml ; DIGESTION TIME(25-30°C) : 15 MIN ; 20% NAPHTHALENE : 2 ml ; SHAKING TIME : 1 MIN
REFERENCE : REAGENT BLANK

3.3 Effect of reagent concentration

Varying amounts of APDC reagent were added to the samples containing 30 μg of iron(III) and 2.0 ml of the buffer solution, and variations in the absorbance of the chelate were studied at 357 nm. The results are shown in Fig.3. It can be seen that the absorbance increased with increasing amounts of APDC solution up to 0.5 ml of 0.2% APDC solution and remained practically constant in the range of 0.5-5.0 ml. Consequently, 2.0 ml of 0.2% APDC solution were added for the further work.

3.4 Effect of buffer solution and digestion time

The various amounts of the acetate buffer solution(pH 5.7) were added to the sample solutions containing 30 μg of iron(III) and 2.0 ml of 0.2% APDC solution, and the adsorption of the chelate was carried out by the procedure. The adsorption of the chelate were not given the effect by the addition of 0.5-5.0 ml of the buffer solution. In the present experiment, 2.0 ml of the buffer solution were used fot the further work. The iron(III) - APDC chelate in the solution containing 30 μg of iron(III) at pH 4.7 was digested at room temperature, and the effect of digestion time on the absorbance was investigated in the range of 1-40 min. The results are shown in Fig.4. The absorbance increased with increasing digestion time up to 10 min, and then was almost constant independently of digestion time in the range of 10-40 min. Consequently, a 15-min digestion time was selected for the further work.

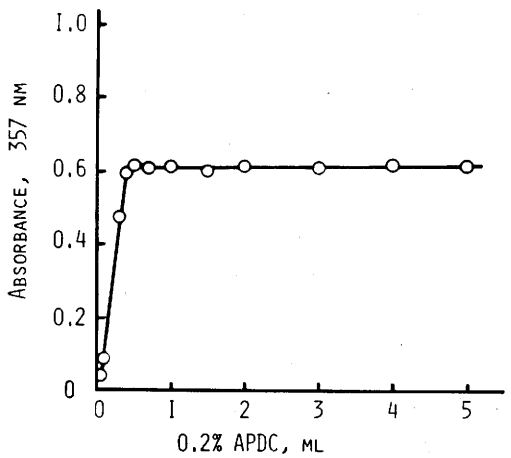

FIG. 3 EFFECT OF REAGENT CONCENTRATION
Fe(III) : 30 μg ; pH : 4.7 ; DIGESTION TIME (25-30°C) : 15 MIN ; 20% NAPHTHALENE : 2 ML ; SHAKING TIME : 1 MIN ; STANDING TIME : 10 MIN
REFERENCE : REAGENT BLANK

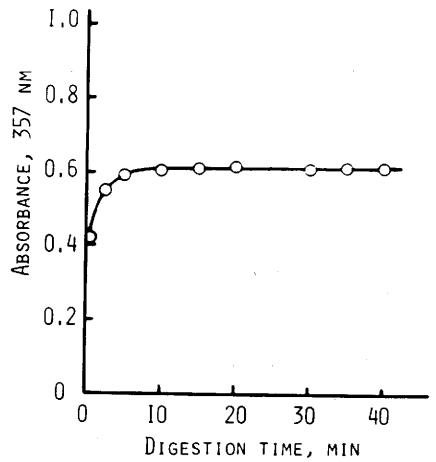

FIG. 4 EFFECT OF DIGESTION TIME
Fe(III) : 30 μg ; pH : 4.7 ; 0.2% APDC : 2.0 ML ; 20% NAPHTHALENE : 2 ML ; SHAKING TIME : 1 MIN ; STANDING TIME : 10 MIN
REFERENCE : REAGENT BLANK

3.5 Effect of naphthalene concentration

Various amounts of naphthalene were added to the sample solution containing the iron(III)-APDC chelate, and the adsorption of the chelate was performed by the procedure. Figure 5 shows the effect of addition of naphthalene on the absorbance. From the experimental data, the addition of 0.5-4.0 ml of 20% naphthalene solution did not cause the effect on the absorbance. Consequently, 2.0 ml of 20% solution were added for the further work.

3.6 Effect of shaking time

The effect of shaking time on the absorbance of the chelate was investigated by the procedure. The results are shown in Fig.6. The adsorption of the chelate onto microcrystalline naphthalene was completed by the vigorous shaking for 20 sec. Consequently, 1 min of shaking time was selected for the further work.

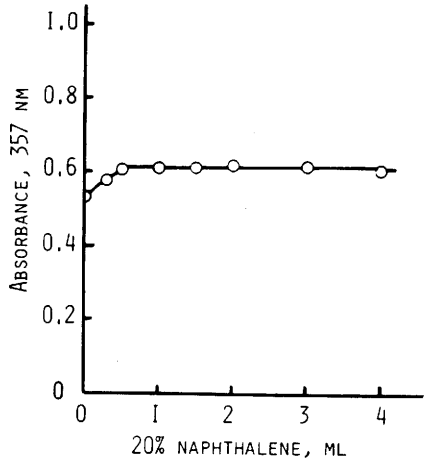

FIG. 5 EFFECT OF NAPHTHALENE CONCENTRATION
Fe(III) : 30 μg ; pH : 4.7 ; 0.2% APDC : 2.0 ml ; DIGESTION TIME(25-30°C) : 15 min ; STANDING TIME :10 ml ; SHAKING TIME : 1 min ;
REFERENCE : REAGENT BLANK

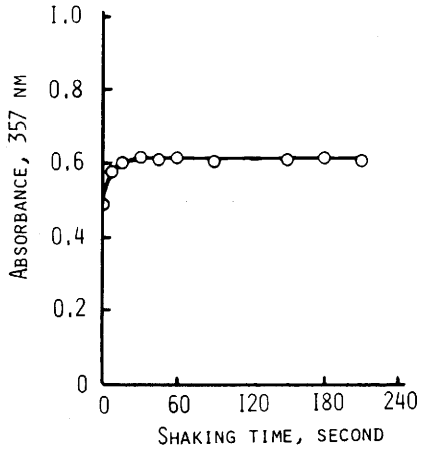

FIG. 6 EFFECT OF SHAKING TIME
Fe(III) : 30 μg ; pH : 4.7 ; 0.2% APDC : 2.0 ml ; DIGESTION TIME(25-30°C) : 15 min ; 20% NAPHTHALENE : 2 ml
REFERENCE : REAGENT BLANK

3.7 Effect of standing time

The adsorbed mixture of the chelate and naphthalene was separated from the solution , dried in a dryer and dissolved in chloroform. The color of the chelate in chloroform solution decreased by less than 4.6% over the range 5-40 min. Consequently, a 10-min standing time was selected for the further work.

3.8 Calibration graph

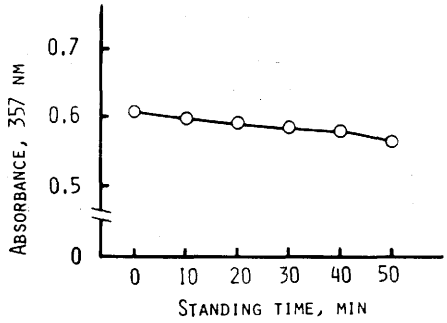

FIG. 7 EFFECT OF STANDING TIME
Fe(III) : 30 ug ; pH : 4.7 ; 0.2% APDC : 2.0 ml ; 20% naphthalene : 2 ml ; Digestion time(25-30°C) : 15 min ; Shaking time : 1 min
Reference : Reagent blank

The absorbances for varying concentration of iron(III) were measured at 357 nm against the reagent blank under the optimum conditions described above. Table 1 shows calibration graph, precision, molar absorptivity and sensitivity for iron(III).

Table 1 Calibration graph, precision, molar absorptivity and sensitivity for iron(III)

(A) Calibration graph for iron(III)

$As = (0.205) \cdot C - (0.005)$

As : Absorbance vs reagent blank

C : μg iron(III), $2.3 \leqq C \leqq 49$

(B) Precision for iron(III)

n = 10, C = 30 μg, C.V. = 1.0%

(C) Molar absorptivity and sensitivity for iron(III)

Wavelength (nm)	Molar absorptivity ($l \cdot mol^{-1} \cdot cm^{-1}$)	Sensitivity ($\mu g/cm^2$)
357	1.1×10^4	4.9×10^{-3}
500	3.7×10^3	1.5×10^{-2}
590	3.7×10^3	1.5×10^{-2}

3.9 Effect of diverse ions

Alkali metal salts and metal ions were individually added to the solutions containing 30 μg of iron(III) and the described procedure was

applied. The analytical data are shown in Table II.

Table II Effect of diverse ions

Ion	Added as	Amounts of ion added	Ion(III) found(μg)	Relative error(%)
—	—	———	30.0	0
Cl^-	NH_4Cl	150 mg	30.0	0
		300 mg	29.3	-2.3
CO_3^{2-}	Na_2CO_3	1.0 mg	30.2	+0.7
"	"	5.0 mg	29.2	-2.7
SO_4^{2-}	$(NH_4)_2SO_4$	150 mg	29.0	-3.3
"	"	300 mg	28.0	-6.7
PO_4^{3-}	$Na_2HPO_4 \cdot 12H_2O$	1.0 μg	30.1	+0.3
"	"	3.0 μg	30.1	+0.3
"	"	10.0 μg	29.4	-2.0
Na^+	NaCl	30 mg	30.5	+1.7
"	"	90 mg	30.2	+0.7
"	"	150 mg	28.6	-4.7
K^+	KCl	30 mg	30.3	+1.0
"	"	150 mg	29.9	-0.3
Ca^{2+}	$CaCl_2 \cdot 2H_2O$	30 mg	29.4	-2.0
"	"	150 mg	30.3	+1.0
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	30 mg	30.1	+0.3
"	"	150 mg	29.8	-0.9
Al^{3+}	$AlCl_3 \cdot 6H_2O$	0.3 mg	30.7	+2.3
"	"	1.5 mg	30.5	+1.7
"	"	3.0 mg	32.8	+9.3
Zn^{2+}	$ZnCl_2$	30 μg	30.4	+1.3
"	"	150 μg	30.1	+0.3
"	"	300 μg	30.8	+2.7
Mn^{2+}	$MnCl_2 \cdot 4H_2O$	30 μg	30.8	+2.7
"	"	150 μg	30.5	+1.7
"	"	300 μg	31.0	+3.3
Pb^{2+}	$Pb(NO_3)_2$	30 μg	29.7	-1.0
"	"	150 μg	31.0	+3.3
"	"	300 μg	32.2	+7.3
Cd^{2+}	$CdCl_2$	10 μg	29.7	-1.0
"	"	30 μg	30.1	+0.3
"	"	90 μg	32.4	+8.0
Cu^{2+}	$Cu(NO_3)_2 \cdot 3H_2O$	3 μg	30.0	0
"	"	5 μg	29.9	-0.4

"	"	10 μg	31.2	+4.0
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	0.5 μg	30.1	+0.3
"	"	2.0 μg	30.1	+0.3
"	"	3.0 μg	31.4	+4.7
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	0.5 μg	30.4	+1.3
"	"	2.0 μg	31.3	+3.7
"	"	3.0 μg	32.8	+9.3

Iron(III) : 30 μg ; pH : 4.7 ; 0.2% APDC : 2.0 ml ; Error $\leqq$ 3%

in the determination of iron(III) was considered tolerable. The tolerance limits, given in mg or μg in parentheses, for cations and anions are : K^+(150 mg), Na^+(150 mg), Ca^{2+}(150 mg), Mg^{2+}(150 mg), Al^{3+}(1.5 mg), Cl^-(300 mg), SO_4^{2-}(150 mg), CO_3^{2-}(5 mg), Zn^{2+}(300 μg), Mn^{2+}(300 μg), Pb^{2+}(150 μg), Cd^{2+}(30 μg), Cu^{2+}(5 μg), Co^{2+}(2 μg), Ni^{2+}(2 μg), PO_4^{3-}(10 μg). The following ions interfered seriously : Cu^{2+}, Co^{2+}, Ni^{2+}, PO_4^{3-}. These metal ions must be preliminary eliminated before adsorption by some methods such as ion-exchange separation, solvent extraction, addition of masking reagent or pH adjustment.

3.10 Iron analysis in standard reference and environmental samples

The present method was used for the determination of iron in standard reference materials(e.g. alloys), metallic aluminum, metallic magnesium and natural water samples. The results were compared with the standard spectrophotometric procedure for iron using 1,10-phenanthroline, as shown in Tables III and IV.

The recommended procedure of samples is as follows :

(A) Aluminum alloy(N.B.S., SRM-85b) : Take 0.8424 g of this alloy and dissolve it in 40 ml of HCl(1+1) and then treat with 2.0 ml of 30% H_2O_2. The excess of H_2O_2 was decomposed by heating the solution on a water bath and the volume completed to 100 ml with double distilled water. A 3-ml aliquot was transfered to a 100-ml separatory funnel containing 25 ml of HCl(1+1), and 25 ml of water were added further. Iron in this sample was extracted with vigorous shaking for 5 min with 20 ml of MIBK. It was extracted again from the organic phase with 25 ml of water and the new procedure was applied for its determination. The same technique was used for other samples.

(B) Copper Silicon(N.B.S., SRM-158a) : Take 0.1086 g of this alloy and dissolve it in 10 ml of HCl(1+1), 10 ml of H_2SO_4(1+1), 1 ml of HNO_3 and 1 ml of 30% H_2O_2. The solution was gently heated on a water

bath. The excess of H_2O_2 and acid was evaporated and then the volume was completed to 200 ml with water. A 5-ml aliquot was used for the procedure.

(C) Metallic aluminum(shot) : A 2.0815 g of aluminum shot was gently dissolved in 90 ml of HCl(1+3) and then treated with 2 ml of 30% H_2O_2. The excess of H_2O_2 was decomposed by heating the solution on a water bath and the volume completed to 200 ml with water. A 2-ml aliquot was used for the present procedure described above.

(D) Metallic magnesium(powder) : A 10.1816 g of magnesium powder was gently dissolved in 150 ml of HCl(1+1) and treated with 5 ml of 30% H_2O_2. The excess of H_2O_2 was decomposed by heating the solution on a water bath and the volume completed to 200 ml with water. A 35-ml aliquot was used for the procedure described.

(E) Natural water samples : Samples were filtered to remove suspended particulates and filtrates were analyzed for the iron content using this method and 1,10-phenanthroline method.

Table III Comparative analysis of iron in reference materials(alloys) and metals

Sample	Composition (%)	Iron, certificated value (%)	Present method (%)	1,10-phenanthroline method (%)
N.B.S. SRM-85b Al alloy	Cu:3.99, Mg:1.49 Mn:0.61, Cr:0.21 Si:0.18, Ni:0.089 Zn:0.03, Ti:0.022 Pb:0.021, Ga:0.019 V:0.006	0.24	0.208 0.228 0.225 0.234 0.230	0.218 0.216 0.216 0.222 0.233
N.B.S. SRM-158a Silicon-Bronze alloy	Cu:90.93, Si:3.03 Zn:2.08, Mn:1.11 Ti:0.96, Al:0.46 Pb:0.097, Ni:0.001 P:0.026	1.23	1.244 1.227 1.244 1.210	1.266 1.294 1.275 1.237
Meatllic Aluminum	——	——	0.150 0.154 0.149 0.152 0.150	0.148 0.145 0.147 0.142 0.142
Metallic magnesium	——	——	0.0021 0.0020 0.0018 0.0017	0.0019 0.0019 0.0019 0.0019

Table IV Analytical results of natural water for iron

Sample	Iron(III), ppb (n=3)	
	Present method	1,10-phenanthroline method
River water 1	137 ± 3 C.V. : 2.2%	146 ± 2 C.V. : 1.4%
River water 2	129 ± 7 C.V. : 5.4%	137 ± 5 C.V. : 3.6%
Lake water	628 ± 7 C.V. : 1.1%	662 ± 11 C.V. : 1.7%
Spring water	82 ± 1 C.V. : 1.2%	76 ± 5 C.V. : 6.6%

0.2% APDC : 2.0 ml ; pH : 4.7 ; 20% naphthalene : 2.0 ml

The analytical results by the proposed method were in good agreement with 1,10-phenanthroline method.

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